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Opportunities in Plutonium Metallurgical Research

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OPPORTUNITIES IN PLUTONIUM METALLURGICAL RESEARCH*

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ABSTRACT

This is an exciting time to be involved in plutonium metallurgical research. Over the past few years, there have been significant advances in our understanding of the fundamental materials science of this unusual metal, particularly in the areas of self-irradiation induced aging of Pu, the equilibrium phase diagram, the homogenization of δ-phase alloys, the crystallography and morphology of the α′-phase resulting from the isothermal martensitic phase transformation, and the phonon dispersion curves, among many others. In addition, tremendous progress has been made, both experimentally and theoretically, in our understanding of the condensed matter physics and chemistry of the actinides, particularly in the area of electronic structure. Although these communities have made substantial progress, many challenges still remain. This brief overview will address a number of important challenges that we face in fully comprehending the metallurgy of Pu with a specific focus on aging and phase transformations.

INTRODUCTION

In 1940, G.T. Seaborg, J.W. Kennedy, and A.C. Wahl created the first man-made Pu at the Cyclotron in Berkeley, California [1]. From this separation-chemistry start to the first 1-gram quantity of metal to long after the end of the Manhattan Project, Pu metallurgical research was motivated by the requirement to produce a product. The production of a large quantity of material took precedence over quality, and there was simply no extra material or time to conduct detailed basic research. From 1945 onward, the focus began to change. A higher level of effort was placed on determining the basic properties of the actinide metals and alloys with a particular focus on the phase diagrams [2-5].

The driving force and motivation for Pu metallurgical research has undergone a remarkable change in direction over the past two decades. The purpose is no longer to produce a large quantity of material, but rather to understand how plutonium's properties might change with age [6-12]. The continuous radioactive decay of Pu produces impurity daughter products and lattice damage that accumulate with age. How the damage introduced by radioactive decay and the resulting impurities affect metallurgical aspects of Pu, such as mechanical properties, phase

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transformations and phase stability, and magnetic properties, are areas of intense research. In spite of these recent research activities, we still do not fully understand the basis of such features as the lattice parameter expansion with time, the volume increase which can be significantly different from that expected from the lattice parameter expansion, the vacancy migration energy, or the mechanism that appears to limit the size of the helium bubbles that form from alpha decay of Pu into U and He.

A second significant challenge involves the phase transformations of δ-phase Pu alloys, in both new and aged materials. Substantial progress has been made in our understanding of the phase diagram [13,14], but details of the thermodynamics and kinetics of low temperature and high-pressure transformations remain unresolved. Advances have been made in our knowledge of the $\delta \rightarrow \alpha'$ isothermal martensitic transformation [15-19], but still much is unknown about the atomistic mechanisms and kinetics of this transformation during temperature or pressure excursions. Even after 32 years, the origin of the double-C kinetics in the published time-temperature-transformation (TTT) diagram [15] remains essentially undetermined.

Advances in experimental techniques, including synchrotron-based studies and electron energy loss spectroscopy in the transmission electron microscope, coupled to enormous increases in computing power have opened the door for more accurate insights into the electronic structure. Today, Pu science is mainly focused on the understanding of the fundamental relationships between electronic structure, crystallographic aspects, phase stability, and the roles of microstructure, impurities, and defects. The purpose of this overview is to highlight a number of the significant challenges in the field of Pu metallurgy. Among the topics to be discussed are the process of aging and the effects on microstructure, and phase transformations and phase stability.

AGING

Research on natural aging of Pu has received significant attention over the past seven years [6-12, 20-26]. Many of these investigations have focused on the natural self-irradiation caused by the decaying Pu isotopes and the resultant age-related changes in the microstructure. Figure 1 shows the predominant radioactive decay mechanism of ^{239}Pu is that of alpha decay, a process that transmutes the Pu atom into a U atom and emits an alpha particle. Alpha decay occurs at a rate of approximately 41 appm/yr (atomic parts per million per year). The ^{235}U recoil, with starting energy of 86 keV, traverses the lattice approximately 12nm and in doing so, creates on the order of 2300 Frenkel pairs. Ninety percent of these defects return to undamaged δ phase lattice sites, leaving approximately 10% remaining in form of free interstitials and vacancies or interstitial or vacancy clusters [6, 9]. A large amount of research from the nuclear reactor community has shown that these microstructural processes ultimately result in property changes that may include an increase in hardness, a reduction in ductility, and void swelling. On the opposite side of the ^{235}U recoil, a 5 MeV alpha particle is ejected and traverses the lattice approximately 10 μm, losing most of its energy to electronic excitations before stopping with the generation of an additional 265 Frenkel pairs. The alpha particle acquires two electrons to become a He atom at a rate of approximately 41 appm/yr. Howell *et al*. [27], using positron annihilation spectroscopy, have shown that He atom immediately finds an unfilled vacancy. At this stage in the process, the helium filled vacancy is mobile and can readily diffuse through the lattice.

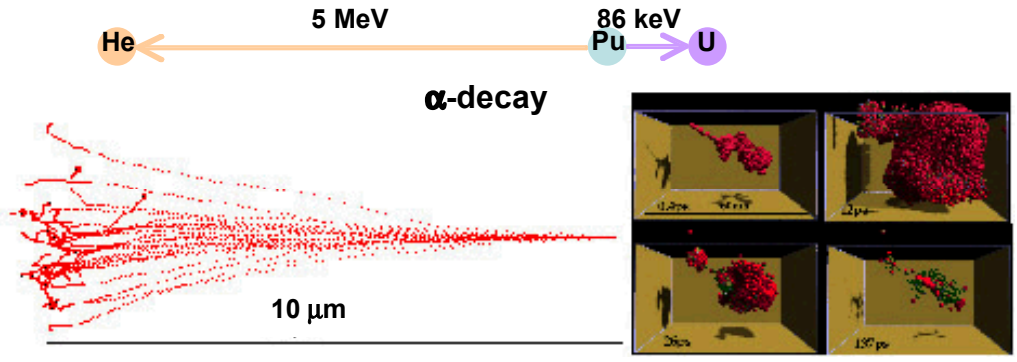

Figure 1. The alpha decay process in Pu. The TRIM simulations on the left shown multiple tracks of the 5 MeV alpha particle as it traverses the lattice and looses its energy to electronic excitations. On the right is a molecular dynamics simulation of the uranium recoil (adapted from reference 9).

There are three aging mechanisms resulting from the alpha decay process that have the potential to cause dimensional changes. These are the initial transient, helium accumulation, and void swelling. The initial transient, first shown in 1976 by Chebotarev *et al*. [28] and later confirmed in 2005 by Oudot [26], is an effect that results in a lattice parameter increase over a period of time between a few months [26] and a few years [28]. The second contributor to dimensional change is the build-up of helium as a result of the alpha decay. Unless the helium escapes from the surface, it must remain in the sample in interstitial positions, in He-filled vacancies, or as He bubbles. Transmission electron microscopy of naturally and accelerated aged samples coupled with rate equation modeling has shown that the vast majority of He is retained as nanometer-sized He bubbles [20]. The third possible age-related phenomenon is void swelling [29], but this has not yet been observed in naturally aged Pu alloys [20] nor been predicted by theory [30].

In order to study aging effects in Pu, scientists at Lawrence Livermore and Los Alamos National Laboratories developed "accelerated aging" alloys. In these materials, 7.3% of the ^{239}Pu atoms are replaced with ^{238}Pu. Because ^{238}Pu undergoes alpha decay approximately 280 times faster than ^{239}Pu, the effective acceleration factor, based upon the starting isotopics and the increase in alpha decay, is about 17 times faster. Thus, scientists can study changes in Pu properties as a function of age in a fraction of the time required to monitor these changes in real-time. Accelerated aging alloys have been particularly useful in long-term investigations of volume changes in aging Pu.

The relationship between volumetric swelling and lattice parameter expansion

Chung *et al*. [25] have used dilatometry to investigate the continuous change in length of an accelerated aging specimen as a function of age. The technique of dilatometry measures the length change of the specimens and takes into account both the increase in volume due to the lattice parameter expansion from the initial transient as well as the free volume increase due to the accumulation of helium. Their results show an approximately 3-month period of rapid volumetric increase followed by a linear regime with a small positive slope.

Two investigations, conducted nearly 30 years apart, show that the lattice parameter of Pu-Ga alloys increases substantially with time at ambient temperature during the early stages of aging [28, 26]. Much of the initial increase is observed to occur during the first 3 months. After approximately 1 year, no more lattice parameter expansion is observed. A comparison of the macroscopic volume expansion measured with dilatometry to the lattice parameter increase measured with x-ray diffraction, reveals a counter-intuitive result; the volume increase measured with x-ray diffraction is much larger than that measured with dilatometry as shown in figure 2.

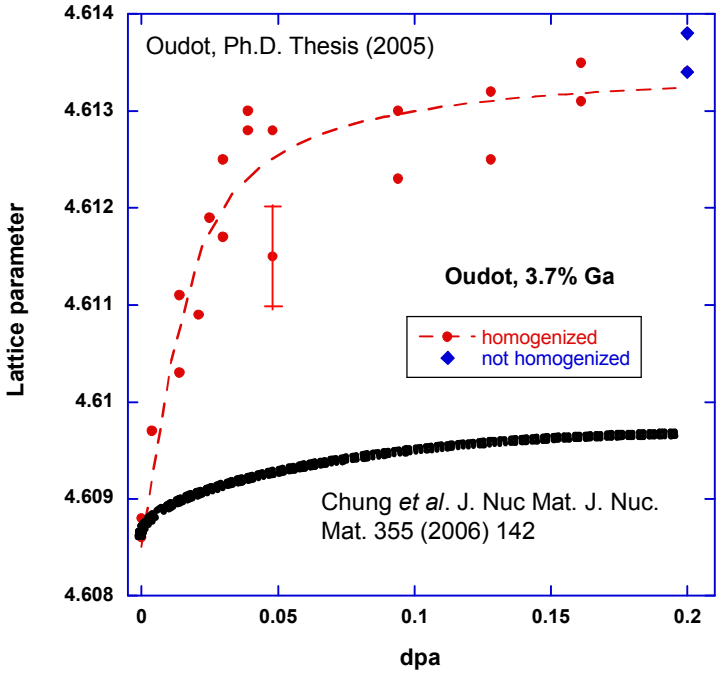

Figure 2. The lattice parameter expansion as measured with x-ray diffraction expansion in terms of displacements per atom (dpa). For these alloys, 1 dpa equals approximately 10 years (adapted from reference 26). The lattice parameter expansion is significantly larger than the volumetric swelling as measured with dilatometry on accelerated aging alloys (adapted from reference 25).

Wolfer *et al*. [22] propose a hypothesis to explain this effect based on the 1964 report by Ellinger, Land, and Struebing [3] that has shown that when Pu is alloyed with Ga, the lattice parameter of the fcc δ phase decreases with increasing Ga content. Wolfer *et al*. suggest that small precipitates of the higher density ζ-Pu_3Ga phase form in the δ matrix as a first stage in the eutectoid decomposition ($\delta \rightarrow \alpha + Pu_3Ga$). In doing so, approximately 10% of the available Ga in the δ phase is removed from the matrix, thus increasing the lattice parameter of the δ phase. Radiation-induced disordering (dissolution) of the ζ-Pu_3Ga phase reaches a steady state leading to the termination of the lattice parameter expansion. So far, this is the only hypothesis to explain the interesting relationship between volume expansion and lattice parameter expansion but there is not yet any experimental evidence to support this. Additional experiments focused on the composition of the matrix and existence of the ζ-Pu_3Ga phase, coupled with first-principles and CALPHAD calculations, are needed.

A second genre of experiments, performed over a 30-year period, reveals a second unexplained phenomenon. Isochronal annealing experiments using electrical resistivity have been used as a method of determining the temperatures where accumulated defects from radiation damage become mobile. Lee *et al.* [31], Elliott *et al.* [32], and Wigley [33] studied the

radiation damage annealing characteristics and reported the isochronal annealing curves of α, δ (Pu-Al samples) and deformed α samples. Fluss *et al.* published isochronal annealing data for a Pu-3.3 at.% Ga alloy that reveal the five stages of annealing [11] and indicate that stage V, the temperature at which vacancy clusters are mobile, is slightly above room temperature. This work suggests that most of the radiation damage should anneal out at room temperature. Thus, annealing slightly above room temperature should remove all of the accumulated radiation damage. However, dilatometry experiments by Kozlov *et al*. on Pu alloys aged naturally [34], and Freibert *et al.* on an alloy isotopically conditioned for accelerated aging [35] at the equivalent of 48 years of natural aging exhibit a volume contraction at ~ 150°C. In addition, Chung *et al*. performed electrical resistivity experiments on naturally aged materials that also reveal a large change in the vicinity of 170°C [23]. Thus, if the radiation damage already anneals out slightly above room temperature, what is the origin of this volume reduction during heating near ~150°C? Could this volume contraction be caused by the ζ-Pu_3Ga phase dissolving back into solution?

The questions here suggest various possibilities of property changes related to the onset of the early stages of the eutectoid reaction, $\delta \rightarrow \alpha + Pu_3Ga$, which have not been considered important in the literature because of the implied long term sluggishness of his reaction (~10,000 years). The recently published "δ conditioning" experiments at 25°C [36] discussed below, and the volume changes and electrical resistivity changes at 150 – 170°C suggest that the eutectoid reaction may be at least a partial reason for these changes, and hence that a pursuit of a much better understood explanation of the kinetics of the eutectoid decomposition is essential.

Helium bubbles

Transmission electron microscopy (TEM) has been applied to the study of Pu alloys since 1967 [37]. However, difficulties with specimen preparation, including the hazardous, toxic, and highly reactive nature of Pu, had precluded observation of age-related defects. Rohr and Staudhammer first reported the observation of He bubbles in a 17 year-old material that had been annealed at 400°C [38]. Annealing at this temperature increased the size of the He bubbles enough to permit observe them on grain boundaries. Recent advances in specimen preparation coupled with a higher energy TEM and an energy filter have allowed us to observe the microstructure, composition, and spectroscopy in naturally and accelerated aged materials [20]. Naturally aged samples ranging from 6 months to 44 years old and accelerated aging alloys up to 65 years old have been characterized, with over 40,000 bubbles counted. A typical micrograph of He bubbles in 42-year old naturally aged material is shown in figure 3a. The average size for naturally aged samples between 16 and 44 years old was determined to be ~ 1.4 nm (figure 3b) with a number density on the order of 1-2 x $10^{17}/cm^3$. The experimental results indicate that the He bubble size appears to increase in the early years of aging then remain constant at ~1.4 nm while the number density continues to increase. The unresolved question is, why does the He bubble size appear to saturate at ~1.4 nm? We have indications from positron annihilation that the bubbles that form in the first few months have a low helium to vacancy (He/V) ratio. This He/V ratio is observed to increase with time and it is believed to reach a level of approximately 2.5. At this point, it is conjectured that the pressure inside the bubble and its associated strain field become repulsive to incoming He-filled vacancies. This size-limiting mechanism would then lead to a constant bubble size and a concurrent increase in the number density.

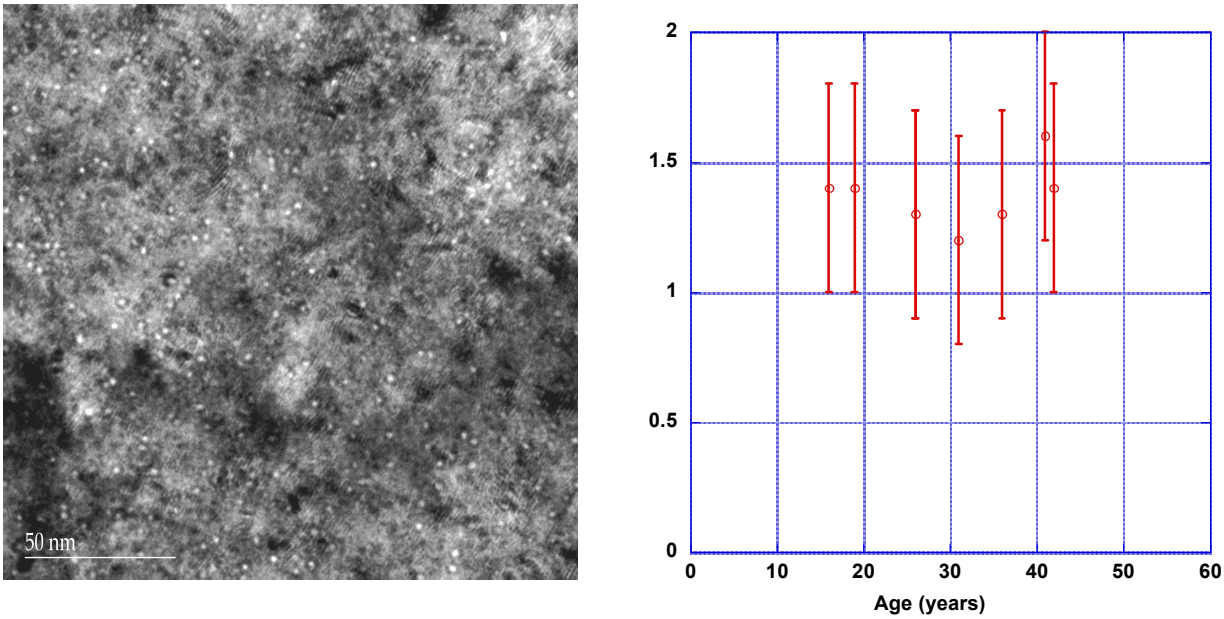

Figure 3. (a) Transmission electron micrograph of He bubbles in 42 year-old material. In the under-focus condition shown here, the bubbles appear as bright dots surrounded by dark rings. (b) Average diameter of the He bubbles as a function of age.

Significant issues in aging

The recent thrust of research focused on Pu aging has improved our understanding of many aspects of the effects of self-irradiation damage on the microstructure and properties. This increased knowledge has also uncovered a number of outstanding challenges, including the counter-intuitive relation between volumetric swelling and lattice parameter expansion, the volume decrease that occurs in the vicinity of 150°C, and the process that appears to lead to a saturation in the He bubble size. Over the past few years, the improved Modified Embedded Atom Method (MEAM) potential within molecular dynamics simulations has been applied to study the cascade damage and properties of He bubbles [39, 40] and density functional theory has been applied to evaluate the effects of actinide daughter products on the stability and lattice parameter of aging Pu alloys and to the propensity for void swelling [21,30]. These computational approaches have furthered our understanding significantly, but continued efforts are needed to resolve these outstanding challenges.

PHASE TRANSFORMATIONS AND PHASE STABILITY

In just the past few years, we have seen the Pu science community converge on an equilibrium composition-temperature phase diagram. For previous decades, researchers in the West followed the Pu-Ga phase diagram published in 1964 by Ellinger *et al*. that reported a region of face-centered cubic δ phase stability extending to sub-ambient temperatures for Ga

contents between approximately 2 and 9 atomic percent [3]. During that same time period, researchers in the former Soviet Union followed the phase diagram published by Chebotarev *et al.* [5] that revealed the likelihood that the δ phase is only metastable at ambient temperatures, and, if it were not for exceedingly slow kinetics, would decompose via a eutectoid reaction to the monoclinic α phase and the compound Pu_3Ga. Although the Chebotarev *et al.* phase diagram showing the eutectoid [5], and the calculation by Adler in 1991 [41] that predicted a eutectoid transformation were available in the West, it was only after the Hecker and Timofeeva publication "A Tale of Two Diagrams" in Los Alamos Science in the year 2000 [14] that increasing worldwide consensus on the eutectoid decomposition has developed. In addition to the phase diagram calculations by Adler using the F.A.C.T. program [41], recent phase diagram simulations by Baskes *et al.* using a Modified Embedded Atom Method potential within a molecular dynamics simulation [42], and by Turchi *et al.* using the CALPHAD program [43] have predicted the eutectoid reaction. The Third Law of Thermodynamics also dictates that a wide solubility δ phase is unlikely to be stable at temperatures near 0K [44, 45].

The $\delta \rightarrow \alpha'$ isothermal martensitic transformation

Faiers *et al.* [46] and Orme *et al.* [15], using a quench and hold technique, were the first to demonstrate that the retained δ phase partially transforms to the α′ phase at subambient temperatures via an isothermal martensitic mode. The monoclinic α′ phase differs from the α phase in that Ga remains trapped in the lattice, which leads to expanded lattice parameters. Although the $\delta \rightarrow \alpha'$ transformation is generally characterized as an isothermal martensitic transformation, it can also be induced and characterized with continuous cooling experiments using techniques such as electrical resistivity, dilatometry, and differential scanning calorimetry (DSC) [17,36,47,48]. The observation that the martensite start (M_s) temperature is a strong function of the Ga content has been shown by Faires *et al.* [46], Orme *et al.* [15], Deloffre *et al.* [49], Hecker *et al.* [47], and others [45]. Adler and Olson have reported that the M_s temperature is a function of grain size; the smaller the grain size, the lower the M_s temperature [50]. Blobaum *et al.* have recently shown that the $\alpha' \rightarrow \delta$ reversion occurs via a burst martensitic mode [17]. The observation of sharp spikes in DSC traces and steps in dilatometry data suggest that the reversion of α′ particles occurs in cascades, with each individual particle reverting nearly-instantaneously and triggering the reversion of neighboring particles.

In performing sequential continuous cooling and heating experiments, Hecker *et al.* [47] and Mitchell *et al.* [51] have demonstrated that the amount of $\delta \rightarrow \alpha'$ transformation in Pu - 1.8 and 2.0 at.% Ga alloys decreases with each thermal cycle even though it appears that all α′ reverts to δ during the heating portion of the cycle. In very recent work, Blobaum *et al.* have shown that the amount of the $\delta \rightarrow \alpha'$ transformation is dependent on details of the thermal cycling [36]. In these experiments, it was reported that, after a cooling and heating cycle, or after a high temperature anneal (375°C), in order to fully reproduce the same amount of transformation on subsequent cooling, the sample must be "conditioned," or annealed, at room temperature for a minimum of 6 hours. Conditioning times shorter than 6 hours produce correspondingly smaller amounts of transformation on subsequent coolings to the transformation temperature range. Other conditioning temperatures were examined in that study, and conditioning at room temperature was found to result in the largest amount of transformation. The authors proposed that α_m embryos might be forming as a precursor to the $\delta \rightarrow \alpha + Pu_3Ga$ eutectoid reaction. These α_m embryos, postulated to have the same composition as the δ matrix, initiate or trigger α′

on subsequent cooling. Appreciating that some processes occur at room temperature is important in experimental metallurgy of Pu, as these experiments nearly always involve some holding at ambient conditions.

Transmission electron microscopy (TEM) and diffraction investigations by Zocco *et al.* [52] have provided extensive insight into the crystallography and morphology of the $\delta \rightarrow \alpha'$ transformation. The orientation relationship between the α' particles and the δ matrix was determined to be $(111)_\delta \parallel (020)_{\alpha'}$ and $[-110]_\delta \parallel [100]_{\alpha'}$. The authors also showed $(205)_{\alpha'}$ twinning as a lattice invariant deformation mode. Moore *et al.* applied dark-field TEM to the partially transformed two-phase structure and showed that the α' particles consist of two variants rotated 60° around the $<020>_{\alpha'}$ direction [19]. High resolution TEM revealed that the α' / δ interface is composed of a terrace and ledge structure that is faceted on $\{111\}_\delta$, in line with the topological model discussed by Hirth *et al.* [18]. A number of studies, beginning with Choudhry and Crocker [53], then Olson and Adler [54], and Jin *et al.* [55] applied theories of martensite crystallography to determine the habit plane of the α' particles in the δ matrix. Most of these studies predicted a $\{123\}_\delta$ habit plane with 24 variants, whereas optical metallography revealed only 4 variants, possibly implying a $\{111\}_\delta$ habit plane. Looking forward, additional TEM experiments, including *in situ* heating and cooling experiments will undoubtedly provide important insights into the transformation crystallography, habit plane, and mechanism.

Double-C curve kinetics

One of the longest standing mysteries in the metallurgy of Pu involves the kinetics of the $\delta \rightarrow \alpha'$ isothermal martensitic transformation as depicted in the experimentally determined time-temperature-transformation (TTT) plots [46, 15]. The TTT diagrams of Pu–0.6 at.% Ga and Pu–0.7 at.% Ga alloys reveal only one C curve, whereas the Pu–1.4 and 1.9 at.% Ga alloys show that there are two separate knees at ~ -130°C and ~ -155°C as shown in figure 4.

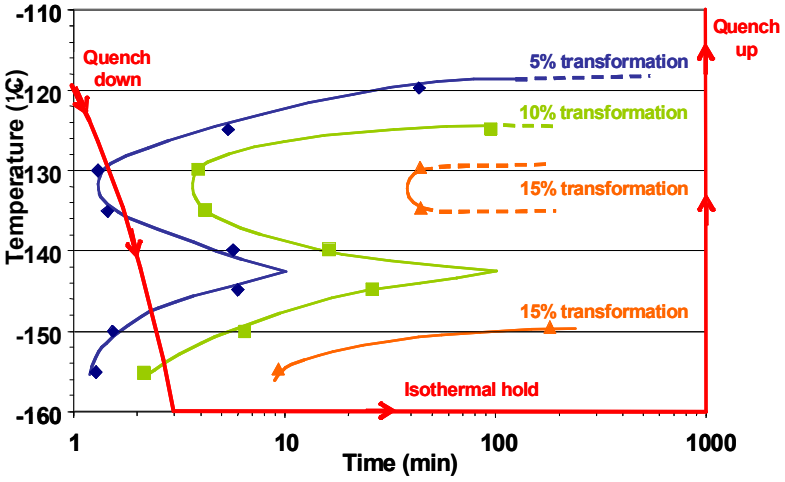

Figure 4. Time-Temperature-Transformation diagram for a Pu-1.9 at% Ga alloy (adapted from reference 15).

Orme *et al.* suggested that the transformation in the upper C was a result of a massive transformation while the lower C was a result of a martensitic transformation [15]. Deloffre reported diffusive and displacive components of the transformation and suggested a change in the mechanism that occurs at ~ 1.5 at.% Ga [49]. The occurrence of the double C implies the possibility of two distinct, thermally activated mechanisms existing for this transformation. Recent DSC work by Oudot *et al.* adds supporting evidence for the double-C behavior and reveals an interesting precursor phenomenon [56]. DSC scans on cooling to a sub-ambient isothermal hold temperature reveal three peaks; the first begins at approximately -103°C, the second at approximately -117°C, and the third at approximately -131°C. A plot of the area of the reversion peak (i.e., the amount of $\delta \rightarrow \alpha'$ reversion) versus isothermal holding temperature reveals two maxima after 18-hours holds at -130°C and -155°C.

Although these experiments shed further light on the kinetics of the transformation, we still do not understand the basic reason for the double-C kinetics. Does it result from different transformation mechanisms, different transformation paths, different morphologies, different embryos or nucleation sites, or something else? Furthermore, how do the kinetics change with age?

The pressure-induced $\delta \rightarrow \alpha'$ transformation

The $\delta \rightarrow \alpha'$ transformation can also be induced by the application of pressure. Under pressure, the $\delta \rightarrow \alpha'$ transformation and reversion characteristics are a strong function of the particular alloying element and its content. A Pu - 2 at.% Al alloy is reported to transform first to β' then to α' under isostatic pressure [57]. Pu - Ga alloys, however, transform directly to α' and undergo either a direct ($\alpha' \rightarrow \delta$) or indirect ($\alpha' \rightarrow \beta' \rightarrow \gamma' \rightarrow \delta$) reversion depending on Ga concentration [47]. Reversion characteristics are remarkably similar to those in the low temperature $\delta \rightarrow \alpha'$ transformations. Why do Pu-Al alloys transform through β' whereas Pu-Ga alloys transform directly to α'? Or do they? Recently, diamond anvil cell experiments by Faure *et al.* on a Pu - 2 at.% Ga alloy reveal a $\delta \rightarrow \gamma' \rightarrow \alpha'$ transformation sequence [58]. In addition, these authors performed time-dependent experiments by pressurizing a specimen to 1.76 GPa and measuring the unit cell volume as a function of time. The volume was observed to decrease over a period of approximately 300 days before reaching a saturation value. This saturation value is close to that obtained by a slow addition of pressure of 0.1 GPa per day. Both of these atomic volumes are greater than that of unalloyed Pu for the same pressure level.

Hecker *et al.* described an experiment in which the lattice parameters of the α' unit cell were measured with x-ray diffraction shortly after a pressure-induced transformation and then approximately one year later [47]. They observed a decrease in the α' unit cell volume over that period and suggested that Ga may be migrating to one of eight unique lattice sites within this monoclinic unit cell. Sadigh and Wolfer performed density functional theory (DFT) calculations in which the molar volume of a Ga atom was determined for each of the eight unique sites of the α' unit cell [30]. The results indicate that indeed the lowest energy configuration for a Ga atom in an α' unit cell is when the atom is located on site 8. Does the time dependence of the α' volume change suggest Ga hopping to site 8? Experimental determination of the Ga occupation on site 8 using techniques such as Extended X-Ray Absorption Fine Structure (EXAFS) may shed some light on these calculations.

Significant issues involved in the δ→ α′ transformation

In recent years, we have gained a reasonable understanding of the eutectoid transformation, the metastability of the δ phase, the crystallography of the α′ phase, and the importance of a conditioning treatment. We have been reminded of the importance of solute homogenization and in turn, have become aware that not all samples reported in the literature have been fully homogenized. However, more work is required to better understand the fundamental science underlying the double-C plots, the mechanism or mechanisms of the δ → α′ transformation and its kinetics, the reason for the precursor phenomenon observed in DSC, δ → α′ transformation under pressure, and the role of site 8 in the α′ structure.

SUMMARY

Great progress has been made in recent years in our understanding of the many metallurgical and electronic structure features of Pu and Pu alloys. These world-wide investigations have led to better understanding of problems resulting from self-irradiation induced natural aging, phase diagram details, and phase transformations. Excellent progress has also been made in the areas of conditioning (annealing) times required for reproducible amounts of low temperature transformation and the burst nature of the reverse martensitic transformation. However, there remain many significant questions that we are now in a position to address with additional experiments and theory. These include:

[1] The counter-intuitive relationship between the lattice parameter expansion and volume swelling with time occurring in Pu-Ga samples in the early stages of aging.
[2] The large volume decrease that occurs at ~150°C.
[3] The helium bubble size reaching an apparent size limit of ~ 1.4 nm.
[4] The explanation of the observed double-C curve kinetics, including the mechanism(s) of transformation, nucleation features, and the interesting precursor phenomenon.
[5] The δ→ α′ transformation under pressure and the formation of an intermediate β phase in Pu-Al alloys, and the γ′ phase in Pu-Ga alloys.

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